

Extraordinary wetting phase diagram for mixtures of Bose-Einstein condensates

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The possibility of wetting phase transitions in Bose-Einstein condensed gases is predicted on the basis of Gross-Pitaevskii theory. The surface of a binary mixture of Bose-Einstein condensates can undergo a first-order wetting phase transition upon varying the interparticle interactions, using, e.g., Feshbach resonances. Interesting ultralow-temperature effects shape the wetting phase diagram. The prewetting transition is, contrary to general expectations, not of first order but critical, and the prewetting line does not meet the bulk phase coexistence line tangentially. Experimental verification of these extraordinary results is called for, especially now that it has become possible, using optical methods, to realize a planar “hard wall” boundary for the condensates.

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In this Letter we pose and answer theoretically the following fundamental questions. Is a wetting phase transition possible in ultra-cold dilute gases which undergo Bose-Einstein condensation (BEC)? How many species of atoms are needed to compose two coexisting phases with an interface? What is the nature of the surface or “wall” at which these phases are “adsorbed”? If a wetting transition occurs, is its character first-order or critical? What is the nature of possible prewetting phenomena away from bulk two-phase coexistence? We focus on the essential physics in the application of wetting theory to BEC and give details of the calculations elsewhere¹.

The simplest system, a one-component gas, is insufficient for studying wetting transitions, because the condensate fraction and the normal fraction are fully mixed in position space. Spatial segregation is only possible in an external potential (e.g., gravity)². Without this potential an interface between normal fraction and condensate does not exist, and therefore the essential interfacial tension is missing.

The next simplest BEC system is a two-component gas. Binary mixtures of trapped BE condensates of alkali-metal atoms have received much attention, experimentally^{3,4} and theoretically^{5,6,7}, since the seminal predictions concerning their phase behavior by Ho and Shenoy⁵. Different degrees of spatial segregation of two pure-component condensates at two-phase coexistence, and the possibility of a symmetric-asymmetric configurational transition in a trap, have been elucidated by Ao and Chui⁶ and Svidzinsky and Chui⁷.

We exploit these findings in the context of wetting phenomena^{8,9,10,11}, and point out the existence of a surface phase transition from partial to complete wetting, upon varying the intra- or inter-species interactions in mixtures of BE condensates. The surface consists of a planar “hard wall”, at which the condensate wave functions vanish.

The basic physics of wetting is best indicated by invoking the familiar energy balance known as Young’s law,

$$\gamma_{W1} = \gamma_{W2} + \gamma_{12} \cos \theta \quad (1)$$

where γ_{Wi} is the surface (free) energy of a phase of pure component i , γ_{12} is the interfacial tension between pure phases 1 and 2, and θ is the contact angle with which the 1-2 interface meets the surface. One of the components, say 2, is preferentially adsorbed at the surface, so that $\gamma_{W1} > \gamma_{W2}$. The surface phase transition from *partial wetting* ($\theta > 0$; Figure 1a) to *complete wetting* ($\theta = 0$; Figure 1b) is then the dramatic phenomenon in which, at the surface, pure phase 1 is displaced by a macroscopically thick wetting layer of pure phase 2. Thus, the W_1 surface is replaced by a W_2 surface in parallel with a 1-2 interface. The physical implications of the singularity structure around wetting transitions have been the subject of impressive experimental¹¹, theoretical¹² and simulational¹³ research.

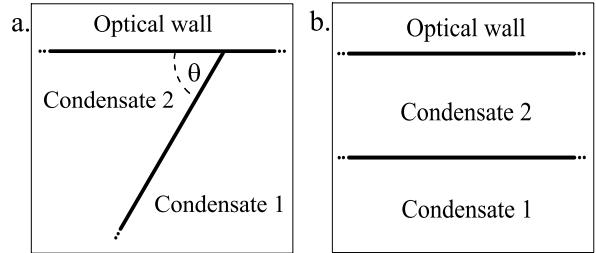


FIG. 1: a) Partial wetting. The interface between the two condensates makes a finite contact angle with the wall. b) Complete wetting. A macroscopic layer of condensate 2 intrudes between the wall and condensate 1.

In view of the ultra-low (typically nanoKelvin) temperature needed for BEC in dilute gases, the quantum mechanical many-body theory at $T = 0$ is appropriate. For weakly interacting gases the Bogoliubov mean-field theory of BEC^{2,14,15} is justified. For our inhomogeneous binary mixture one obtains two coupled Gross-Pitaevskii (GP) equations for the condensate order parameters $\psi_1 = F_1 e^{i\chi_1}$ and $\psi_2 = F_2 e^{i\chi_2}$. We recall that ψ is the ground state expectation value of the Boson field operator. It can be chosen real here, since stationary (non-flowing) condensates are assumed, so $\chi_1 = \chi_2 = 0$.

We adopt the standard geometry for wetting and confine the atoms to the half-space $z > 0$. The relevant surface is the $z = 0$ plane. It is then natural to employ the grand canonical ensemble, with chemical potentials μ_1 and μ_2 ¹⁶. The GP equations are the Euler-Lagrange equations of the grand potential functional

$$\Omega[\psi_1, \psi_2] = \int_{z \geq 0} d\mathbf{r} \sum_{i=1,2} \left(\psi_i(\mathbf{r})^* \left[-\frac{\hbar^2}{2m_i} \nabla^2 - \mu_i \right] \psi_i(\mathbf{r}) + \frac{G_{ii}}{2} |\psi_i(\mathbf{r})|^4 \right) + G_{12} |\psi_1(\mathbf{r})|^2 |\psi_2(\mathbf{r})|^2 \quad (2)$$

The sum is over the two species, with atomic masses m_i . The repulsive interactions $G_{ij} > 0$ are related to the s -wave scattering lengths a_{ij} through $G_{ii} = 4\pi\hbar^2 a_{ii}/m_i$ for like particles and $G_{12} = 4\pi\hbar^2 a_{12}(1/m_1 + 1/m_2)$ for unlike particles. For alkali-metal atoms, $a \approx 10^2 \text{ \AA}$.

The confining potential is taken to be a hard wall at $z = 0$, so that

$$\psi_1(x, y, 0) = \psi_2(x, y, 0) = 0 \quad (3)$$

The closest experimentalists have come to make a hard wall is to use an evanescent wave, blue-detuned, extending from within a planar prism¹⁹. The turn-on distance of this optical wall is typically only about $\lambda/2\pi \approx 80 \text{ nm}$. To contain the atoms, a conventional quadratic-confining magnetic trap can be added, so that a “quasi-square” exponential potential results for $z < 0$, and the usual $ax^2 + by^2 + cz^2$ for $z > 0$. In order for volume forces due to a non-uniform external potential to be negligible compared to surface forces governing wetting, the harmonic potential must be sufficiently flat-bottomed near $\mathbf{r} = 0$. For a characteristic length of the order of microns or longer we can ignore the harmonic potential in the calculations and assume translational invariance of ψ in x and y directions.

The known condition for bulk phase separation of the binary mixture is that the unlike particles repel each other more strongly than the like ones on average, $K \equiv G_{12}/\sqrt{G_{11}G_{22}} > 1$. Otherwise, a single mixed phase results. Bulk phase coexistence requires equal pressure, $P_1 = P_2$, in the two phases, with $P_i = \mu_i/2G_{ii}$. A *bulk triple point* with coexisting mixed and pure phases 1 and 2 is found for $K = 1$. This triple point bears a reminiscence to a critical point in that the interfacial tension between pure phases 1 and 2 vanishes. However, the phases themselves remain distinct.

The bulk condensate number densities in the pure phases are $\rho_{0i} \equiv |\psi_i(\infty)|^2 = \mu_i/G_{ii}$. A “healing length” $\xi_i = \hbar/\sqrt{2m_i\rho_{0i}G_{ii}}$ characterizes the recovery distance of the order parameter from a disturbance, e.g., a surface where $\rho = 0$. A typical value is $\xi \approx 10^3 \text{ \AA}$. The two surface grand potentials γ_{w_i} are proportional to the product of the pressure and this healing length¹⁴, $\gamma_{w_i} = (4\sqrt{2}/3)P\xi_i$, which defines a surface “thickness”.

For strongly repulsive interactions and/or high densities, the healing length of a condensate is short, and its surface tension is low, so that it prefers to be near the surface. This suggests to define a “surface field” proportional to the difference $\xi_1 - \xi_2$.

The second important length is the “penetration depth” Λ , characterizing the distance over which one condensate decays or “penetrates” into the other at the 1-2 interface⁶, $\Lambda_i = \xi_i/\sqrt{K-1}$. A typical value is $\Lambda \approx 1 \mu\text{m}$. This length diverges when approaching the triple point. Ao and Chui discuss the following two limits for which we determine the wetting behavior.

A) Strong segregation limit: Partial Wetting

In the limit $\Lambda \ll \xi$ or $K \rightarrow \infty$ the condensates show almost no mutual penetration. The interface then consists of two surfaces, one where condensate 1 decays to zero over the healing length ξ_1 , and an adjacent one where condensate 2 vanishes over ξ_2 . The interface thickness is thus $\xi_1 + \xi_2$ and its tension is approximately $\gamma_{12} \approx \gamma_{w_1} + \gamma_{w_2}$. There can be no complete wetting, since the energy cost of an interface is too high to be able to satisfy Young’s law with $\theta = 0$.

B) Weak segregation limit: Complete Wetting

In the experimentally more relevant limit $\Lambda \gg \xi$ or $K \rightarrow 1$ the mutual penetration of the condensates leads to mixing on the scale of $\Lambda_1 + \Lambda_2$. In spite of its huge thickness, the interface has a low tension, since the energy per unit volume scales as^{1,6} $(\xi/\Lambda)^2 P$. As a result¹⁷, $\gamma_{12} \propto P(\xi_1 + \xi_2)\sqrt{K-1}$. The interfacial tension vanishes at the triple point with a square-root singularity. For Young’s contact angle we obtain

$$\cos \theta = \text{const.} \left(\frac{\xi_1 - \xi_2}{\xi_1 + \xi_2} \right) (K-1)^{-1/2} \quad (4)$$

This implies that a wetting transition is unavoidable upon approach of the triple point. Indeed, the wetting phase boundary implied by (4) is given by

$$(\xi_1/\xi_2 - 1) \propto (K-1)^{1/2} \quad (5)$$

A full numerical computation¹ corroborates the physical insights gained so far, and leads to the wetting phase diagram at bulk two-phase coexistence shown in Fig.2. The wetting transition is of *first order*. On the phase boundary the grand potential of partial wetting crosses that of complete wetting, and both states have metastable continuations. Interestingly, at the wetting transition the grand potential is degenerate: all wetting layers have the same energy, regardless of the layer thickness. This is akin to what happens at the wetting transition in an Ising model at $T = 0$, where the interface consists of a plane of broken bonds at an arbitrary distance from the surface. The usual entropic repulsion between the surface and the interface due to interfacial capillary wave fluctuations is absent at $T = 0$.

Yet, in contrast with Ising spins on a lattice, the continuum field theory we are dealing with allows one to “inflate” a wetting layer by varying its shape and thickness continuously between infinitesimal and macroscopic,

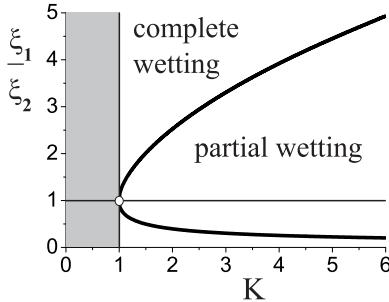


FIG. 2: Wetting phase diagram in the plane of surface field $(\xi_1 - \xi_2)/\xi_2$ and relative interaction strength K . At bulk two-phase coexistence ($K > 1$) a first-order phase boundary separates partial wetting from complete wetting, for $\xi_1/\xi_2 > 1$. For $\xi_1/\xi_2 < 1$ the roles of the condensates are interchanged and one may use “drying” in place of “wetting”. The phase boundary is parabolic near the triple point $(1, 1)$.

at *constant* grand potential. A remarkable consequence of this is the coincidence, at bulk two-phase coexistence, of *nucleation* and wetting transitions¹. For illustration, Figure 3 shows two order parameter profiles for parameters K and ξ_1/ξ_2 on the wetting line.

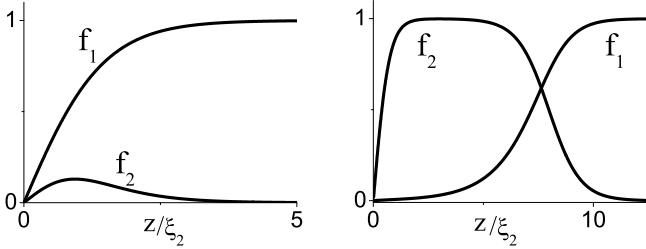


FIG. 3: Inflation of a wetting film of condensate 2 at the surface of condensate 1. Normalized order parameters, $f_i \equiv F_i/\sqrt{\rho_0 i}$, are shown for two surface states with the same grand potential, at first-order wetting ($K = 1.5$, $\xi_1/\xi_2 = 2$).

A crucial physical question is how the surface field and/or the relative interaction strength can be tuned experimentally. Importantly, these variables can be expressed in terms of the atomic masses and scattering lengths alone, and are therefore fully microscopic. Feshbach resonances allow manipulation of the scattering length(s) over more than an order of magnitude¹⁸ and are a suitable tool for exploring the phase diagram.

Away from bulk two-phase coexistence, a first-order wetting transition normally possesses an extension into the bulk one-phase region where the wetting phase is metastable. If this extension exists, general arguments show that it must also be of first-order, at least from the wetting point up till a prewetting (multi-)critical point in the phase diagram. Furthermore, the prewetting line must meet the bulk two-phase coexistence line tangentially²⁰. To our knowledge, in all systems that have been observed or predicted to undergo a first-order wetting transition, ranging from classical adsorbed

fluids¹¹ or superfluids¹⁰, over magnetic systems¹³, to type-I superconductors²¹, the prewetting transition is also of first order. Yet, mixtures of BE condensates provide us with an exception, as we now show.

Figure 4 shows the prewetting phase diagram in the space of “bulk field” and relative interaction strength K . The bulk field which can drive the mixture away from bulk two-phase coexistence is proportional to the pressure difference $P_1 - P_2$. The combination $\sqrt{P_1/P_2} - 1$ serves the same purpose. Note that pure phase 1 (2) is stable in bulk for $P_1 > (<)P_2$ and that the mixed phase is stable for $K < \min\{\sqrt{P_1/P_2}, \sqrt{P_2/P_1}\}$. The bulk triple point is at $(1, 1)$. For a given value of the surface field, i.e., for fixed ξ_1/ξ_2 , the wetting point W and the prewetting line are shown. When, along the path indicated by arrows, the prewetting transition is crossed, an infinitesimal film of condensate 2 is nucleated at the surface of condensate 1. Moving further to the left, the thickness of this film grows and, upon approach of two-phase coexistence (at $P_1 = P_2$), it diverges logarithmically. This slow divergence is expected for the approach to *complete wetting* in systems with short-range interactions. The extraordinary physics emanating from this phase diagram concerns i) the second-order or “critical” nature of the entire prewetting line, and ii) the fact that the prewetting line meets bulk two-phase coexistence at a finite angle (clearly seen from the mathematical continuation along the dashed line).

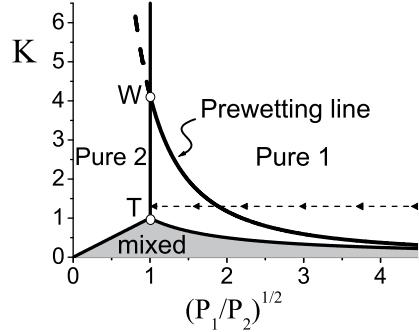


FIG. 4: The phase diagram for prewetting at $\xi_1/\xi_2 = 4$, in the space of relative interaction strength K and bulk field $\sqrt{P_1/P_2} - 1$. The bulk phases “pure 1”, “pure 2” and “mixed” coexist at the triple point T . Bulk two-phase coexistence of the pure condensates is along the line $P_1 = P_2$, on which the first-order wetting transition W is indicated. The second-order prewetting phase boundary intersects the bulk transition at W . The line with arrows indicates a possible approach to complete wetting.

If there is nothing wrong with the general thermodynamic arguments concerning prewetting, how is this anomaly possible? There are two premises in the general reasoning, which are *not* fulfilled here. Firstly, at this first-order wetting transition there is no abrupt jump of the film thickness between a microscopic and a macroscopic value, but all intermediate values are equally stable due to the grand potential degeneracy. Since there is

no interface potential barrier, for consistency the prewetting transition must be continuous instead of first-order, and we find that it is. Secondly, since this prewetting transition is a second-order nucleation transition, unlike for ordinary prewetting, the difference in adsorption on either side of the transition does not diverge upon approach of the wetting transition at W , and the condition for a tangential meeting is not met. Consistently, we find an intersection at a finite angle.

Within the wetting phenomenology we reinterpret the interesting symmetric-asymmetric (SA) transitions predicted for an axially symmetric square-well trap⁶, and for a conventional quadratic magnetic trap⁷. In the symmetric (S) state the condensates form concentric clouds. This corresponds to complete wetting (Fig.1b), with, e.g., a W_2 surface and an embedded 1-2 interface in a “cherry” configuration. This state may exchange stability with one (A) which breaks the trap symmetry, with a planar 1-2 interface cutting across the system. This is partial wetting (Fig.1a).

For a square-well trap, a surface energy balance determines the SA transition⁶. However, it is not governed by Young’s law, but by finite-size effects, cylindrical geometry and particle number conservation. Consequently, the contact angle at the SA transition does not tend to zero continuously as in the *bona fide* wetting transition. Instead, it jumps from a finite value θ_{SA} to zero. For a

quadratic trap, surface and volume contributions are entangled in the energy balance⁷. In the S state the component with the largest self-repulsion is on the outside. For sufficiently small trap radius, an A state is favored, to relieve the high capillary pressure across the curved 1-2 interface in the S state. The wetting interpretation is complicated here due to the spatially varying external potential and the absence of an articulated surface.

In conclusion, in view of the extraordinary ultralow-temperature effects in the predicted wetting phase diagram for binary mixtures of Bose-Einstein condensed gases, we advocate an experimental study of wetting and prewetting in a trap which is suitable for observing true wetting singularities. The confinement should consist of a half-space with one planar “hard wall”, i.e., a steep repulsion with a turn-on length smaller than the healing lengths and penetration depths of the condensates. A mild conventional trap may be used to keep the gas near the wall. The wetting transitions can be induced by tuning the interatomic scattering lengths using Feshbach resonances.

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¹⁶ Calculations for the canonical ensemble, with constrained numbers of condensate atoms N_1 and N_2 were also performed¹. Canonical surface and interfacial energies are

smaller than their grand-canonical counterparts by a factor of 4. The contact angle and wetting phase boundary are ensemble-independent.

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